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1974
1975

1

1976
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Respectfully submitted,

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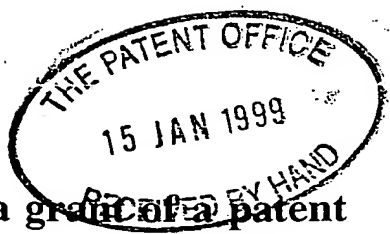
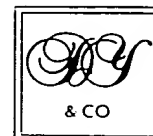
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3. Full name, address and postcode of the or of each applicant
(underline all surnames) IMPERIAL COLLEGE OF SCIENCE,
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SHERFIELD BUILDING
EXHIBITION ROAD
LONDON
SW7 2AZ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4033452001

4. Title of the invention MATERIAL DEPOSITION

5. Name of your agent (if you have one) D YOUNG & CO
"Address for service" in the United Kingdom to which all correspondence should be sent
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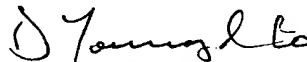
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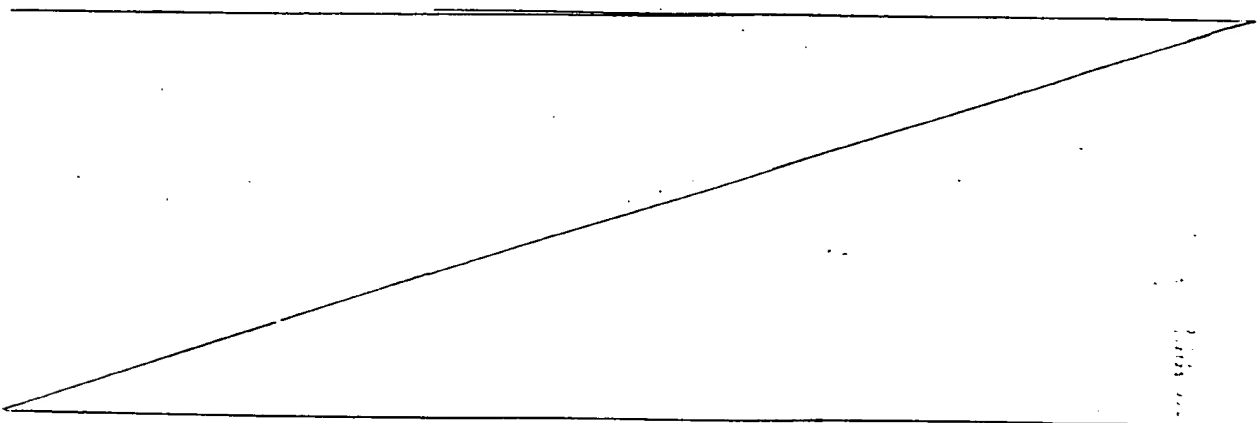
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Material Deposition

This invention relates to material deposition.

Background of the Invention

Ceramic films have found wide application in both structural and functional areas. However, different applications often require films with different thickness. There are no universal coating or film deposition techniques which can cover thin ($<1\text{ }\mu\text{m}$) and thick (e.g. $>10\text{ }\mu\text{m}$) film range. Generally, vapour processing (including chemical vapour deposition, CVD and physical vapour deposition, PVD) has been used to fabricate thin films because of their slow growth rate and expansive equipment. Any attempts to fabricate thick films with large areas have been proven costly and time-consuming. Sol-gel processing can also be used to fabricate thin films. The film thickness is normally below $1\text{ }\mu\text{m}$ on a single coating procedure. Otherwise, thicker film will result in cracking problem. Other chemical methods such as spray pyrolysis have been employed to fabricate both thin and thick films. But the deposition efficiency is low because of the loss of the aerosol precursor to the surrounding, which tends to hinder the low-cost processing advantage, especially for the use of expensive precursors. Moreover, spray pyrolysis has difficulty to deposit very thick films (e.g. $>150\text{ }\mu\text{m}$). A novel method which is called electrostatic spray assisted vapour deposition (ESAVD) technique has



been developed recently by Choy et al. [PCT/GB96/03105, WO97-21848]. The ESAVD process involves spraying atomised precursor droplets across an electric field where the droplets undergo combustion and chemical reaction in the vapour phase near the vicinity of the heated substrate. This produces a stable solid film with excellent adhesion onto the substrate in a single production run and is a more cost-effective method.

However, problems have been found in ESAVD associated with capillary-plate configuration as shown in Fig. 1. These include:

- Deposition rate is limited by the flow rate of the precursor solution through the capillary. For example, for a needle with diameter of 100 μm and 375 μm , the highest possible flow rate achievable is about 15 cc/hr and 50 cc/hr, respectively. As the result of slow flow rate of the solution, the deposition rate is, for example, normally under 20 $\mu\text{m/hr}$ for the deposition of dense CdS film. Of course, the deposition rate could be higher for the deposition of porous films. Also, the deposition rate is depending on the nature of the precursor used, processing conditions etc. Though the flow rate could be increased by increasing the capillary size, the droplet size will increase accordingly, which will affect the coating uniformity and film quality.
- The droplet size distribution via capillary-plate configuration is generally broad. Some larger droplets will form powders during film deposition. It is difficult to obtain totally powder-free films.
- The electrical potential is critical in the effective atomisation to break down the droplet size to the micrometer range. Apart from the limited increase of electrical potential by increasing the high voltage, the distance between the capillary needle and plate is also important. For most of the precursor solutions, the distance, for example, need to be below ~30 mm at 5 to 20 kV for the capillary size of 100 to 500 μm to achieve the corona

discharge. While for some film deposition which require relatively high deposition temperature (e.g. $>600^{\circ}\text{C}$), precipitate will likely be formed in the needle thus block the passage of the precursors because of the high temperature radiation to the capillary.

- Electrostatic atomisation via capillary-plate configuration has specific requirements for the spray solution (e.g. conductivity, surface tension, viscosity, dielectric constant, etc.). For aqueous solution, the precursors used are normally ionic compounds such as nitrates and chlorides, they dissolved well in water, resulting in a high conductivity of the solution (e.g. $> 10^{-1} \text{ S/m}$), which is too high according to Grace & Marijnissen [1994]. The simple-jet mode is likely to occur for high conductivity liquids (see Fig. 1 a). The liquid droplets can be broken down more easily to form ideal cone-jet mode for film deposition using low conductivity liquid (see Fig.1 b). While most of the organic solvents have relatively low conductivity (e.g. $< 10^{-5} \text{ S/m}$) and the chemical precursors are normally of low-conducting (e.g. acetylacetonate or alkoxide etc). Therefore, the precursor solutions used successfully in ESAVD process are mostly non-aqueous systems. The use of ESAVD might be difficult for the deposition of dense films from aqueous precursor systems.

It has been known for a long time that aerosol generated by ultrasonic atomisation have a very narrow droplet size distribution and the size can go down to $1 \mu\text{m}$ depending on the frequency of the ultrasonic generator [Blandenet, et al., 1981]. Spitz and Vigue [Br. Patent 1362803, 1971] reported the use of a 'pyrosol' method for thin film deposition. They utilised an ultrasonic generator to produce the aerosol and then transport them to a heated substrate with the aid of a carrier gas. Various thin films have been fabricated by this method, but the deposition efficiency of the method is relatively low because of the escape of the aerosol stream to the surrounding being deflected and reflected from the substrate. The typical deposition rate is below $3 \mu\text{m/hr}$. The best deposition efficiency for 'pyrosol' process is about

30% [Dutta, et al., 1995]. Siefert [1984] proposed a corona spray pyrolysis method in which the generated aerosol is corona discharged and transported in an electric field towards a heated substrate in the direction of gravity. The discharge electrode is arranged with two tips by an angle of 40-45°. A deposition efficiency of more than 80% was achieved. Only organic precursor solution was used to deposit In_2O_3 and SnO_2 thin films. Powdery precipitate was obtained during deposition of In_2O_3 film probably because of the inadequate temperature field control which led to the homogeneous reaction in the vapour space resulting in the powder formation [Siefert, 1984]. Blandenet [EP 0103505, 1984] reported the use of a mesh-multiple point configuration or an elongated and narrow metallic tube-plate configuration to discharge the aerosol. But the deposition was carried out at room temperature or the substrate was heated beforehand. The precursor films deposited were in a gel or amorphous state. Thin ceramic films were derived from the subsequent post heat-treatment of the as-deposited precursor films at higher temperatures. Because the distance between the mesh and electrode point was large (12 cm), the voltage required was very high (90 kV). The precursor used was mostly metal-organic solution.

In the following pages, references to the "invention" should be read as references to "at least preferred and non-limiting embodiments of the invention".

The aim of this invention is to provide a low cost and high deposition efficiency method for the preparation of both thin and thick films. This method overcomes the disadvantages of the 'pyrosol', ESAVD, Siefert's and Blandenet's methods. The invention proposes a method, termed Electrostatic Assisted Aerosol Jet Deposition (EAAJD), whereby the precursor solution is atomised using an ultrasonic generator to form aerosol which is transported preferably upwards with or without a carrier gas and charged by an electrostatic field between the source and the substrate using a special nozzle design during the deposition to ensure

uniform coating on a heated substrate. This novel method is different from the ESAVD method whereby the dual-function of the capillary-plate configuration in ESAVD method for atomisation and deposition, which is very likely to lead to non-uniform coating, is separated in the EAAJD. Unlike in the ESAVD, both aqueous and non-aqueous precursor solutions can be used in the EAAJD. It is possible to overcome the problems found in the ESAVD method, and to achieve higher deposition efficiency than 'pyrosol' method because of the surface charge of aerosol in the electrostatic field. Unlike Blandenet's method, solid or crystalline films can be produced in a single run on the heated substrate using the EAAJD without the need for further heat treatment. Both aqueous and non-aqueous chemical precursor solutions, or even colloidal sol solutions, can be used in the EAAJD. Aerosol generated by ultrasonic wave is of narrower droplet sizes. The aerosol is transport upwards instead of downwards used in the Siefert's method towards the heated substrate under the electric field, which can prevent dripping on the films and ensure more desirable temperature gradient near the surface of the substrate. The upward electrostatic field assists in a more uniform and efficient deposition. Moreover, this invention uses a special design of aerosol nozzle (see example in Fig.4) which is different from that used by Siefert [1984]. The nozzle used in the EAAJD will enable further breakdown of the aerosol and prevent the decomposition of precursor prematurely. The films deposited using the EAAJD are expected to be of more uniform microstructures. For the large area or curve substrate deposition, a computer controlled X-Y or X-Y-Z table can be used to move the aerosol nozzle and/or the substrate.

Detailed Description of example and non-limiting embodiments

Fig: 2 describes an example of the general set-up of EAAJD for relatively small area deposition. Substrate (4) is positioned on a rotary holder (1) inside a tube furnace. The

position of the holder can be adjusted to a different temperature zone. Aerosol is generated using an ultrasonic generator (7), where both aqueous and non-aqueous precursor solutions can be excited by a piezoelectric transducer (8) through a transfer media (e.g. water) (9). A liquid level controller (10) is used to ensure the constant volume of precursor liquid in the container to achieve constant volume averaged energy dissipation at all time. The aerosol generated is transported by blowing air or carrier gas (e.g. N_2 , Ar, O_2 , NH_3 , H_2S) to the aerosol nozzle (5). A low-pressure environment or vacuum can also be used in the deposition chamber to maintain the aerosol flowing. An electric field is established between the nozzle and the substrate by a high voltage generator (3) (e.g. 10 to 30 kV).

Fig. 3 shows an example of the set-up of EAAJD for relatively large area deposition. The substrate (4) is mounted on a heated substrate holder (1,2) surrounded by insulating material (3). Substrate heating can be achieved by either using contacting heating (e.g. resistance) or non-contacting heating (e.g. IR lamp) methods. A high voltage (5) is placed between the aerosol nozzle (6) and the substrate holder (2). The aerosol (7) is generated by ultrasonic agitation as described in Fig. 2. The aerosol nozzle is fixed on an X-Y or X-Y-Z table (8). Films with large area or curved substrate can be deposited by moving the aerosol nozzle using a computer-controlled X-Y or X-Y-Z table. Multiply nozzles can also be used for large-area deposition and coating onto complex-shaped engineering components. The substrate can be fixed, translated and/or rotated.

Fig. 4 shows an example of the aerosol nozzle structure which is composed of a co-axial tube and a metallic electrode. The tube can be made preferably using non-conducting materials, such as glass, quartz or ceramic which can meet different temperature requirement. The electrode can be conducting materials, such as stainless steel or tungsten wire with single or

multi-tips as shown in Fig. 4 (a) and (b) respectively. The electrode is positioned on a conducting (e.g. stainless steel or aluminium or Indium Tin Oxide (ITO) coated glass) plate with multi-holes.

The advantages of the above EAAJD technique over the existing deposition methods are as following:

1. High deposition efficiency. Since the aerosol droplets become charged and directed by an aerosol nozzle, unlike the 'pyrosol' method, the loss of the precursors to the surrounding is minimised. Deposition efficiency as high as 90% or higher can be achieved. This is not only reduces the cost of the film production but also minimises the pollution from any possible harmful or corrosive starting materials.
2. High film deposition and growth rate. Since less restrictions for ultrasonic aerosol generation than the electrostatic atomisation used in ESAVD technique, the aerosol generating rate in this novel EAAJD method can be higher (e.g. ≥ 5 cc/min) using ultrasonic generator, depending on the precursor solution and agitation power. Growth rate of dense film as high as 1~2 $\mu\text{m}/\text{min}$ or higher can be achieved. Also high deposition rate for large areas and complex shaped components can be achieved using the EAAJD method, for example, by moving the aerosol nozzle on an X-Y or X-Y-Z table, and/or moving the substrate.
3. Single deposition step. Ceramic films can be deposited on a heated substrate in a single run. Unlike Blandenet's method, no post heat-treatment is necessary. Heating can be achieved by either contacting (e.g. resistance heating) or non-contacting (e.g. IR) heating methods.
4. Excellent film adhesion. The aerosol jet of charged droplets hit the substrate and discharged on the counter-charged substrate in a very high velocity and/or

vaporised/decomposed near the vicinity of the heated substrate depending on the material system and deposition conditions. The adhesion of film formed on substrate is excellent comparing to the 'pyrosol' method.

5. Uniform film structure. The aerosol generated by ultrasonic generator (e.g. 1.7~3 MHz) is of fine droplet size ($< 2\mu\text{m}$) and narrow size distribution. The as-deposited film has more uniform structure with smooth surface morphology than the ESAVD method etc.
6. Versatility. The precursor solution can be either aqueous or non-aqueous since both can be excited by ultrasonic agitation to produce aerosol. The solvent for non-aqueous solution is preferably acetylacetone, methanol or 2-methoxyethanol according to their ability to generate aerosol under ultrasonic agitation. Also, the carrier gas can be either non-reactive (e.g. O_2 , air, or N_2) or reactive (e.g. NH_3 or H_2S) depending on the chemical precursor and material systems that are of interests.

EXAMPLES

Example 1

0.01 M aqueous solution of Cadmium chloride and thiourea was used as the chemical precursors for the CdS film deposition. 50 ml of the aqueous solution was put in the ultrasonic container and agitated at a frequency of 1.7 MHz with a power of 50 W and air flow rate of 50 ml/min. The deposition was carried out using a set-up as shown in Fig. 3. The set temperature for glass substrate was 450°C . The distance between the aerosol nozzle and the substrate was 2 cm and the set voltage was 10 kV. The deposition time was 5 minutes. About $1\mu\text{m}$ thick, dense and crystalline CdS films with smooth and uniform surface and columnar structure was deposited as shown in Fig. 5.

Example 2

Commercial colloidal silica solution (Ludox, Dupont, USA) for the deposition of SiO_2 film was diluted with distilled water to an aqueous solution with a concentration of 0.1 g/ml. The aerosol was generated at a frequency of 1.7 MHz with a power of 20 W and air-flowing rate of 50 ml/min. The film was deposited using the set-up as shown in Fig. 3 at a nozzle-substrate distance of 2 cm and 10 kV. The deposition temperature and time was 200°C and 1 minute respectively. Porous SiO_2 film with reticular structure was formed as shown in Fig. 6.

Example 3

A non-aqueous precursor solution for the deposition of BaZrO_3 film was prepared as following. Barium metal (Aldrich) was allowed to react with 2-methoxyethanol (Aldrich) by stirring at room temperature to form barium alkoxide. After the barium metal dissolved completely, a stoichiometric amount of zirconium n-propoxide (70wt% solution in n-propanol) (Aldrich) was added to the barium methoxyethoxide solution and reflux/distil at the boiling point of 2-methoxyethanol (124°C) for 5 hours. Then the final volume of yellow-coloured solution was adjusted using 2-methoxyethanol to make a 0.05M precursor solution. The film was deposited using a set-up as shown in Fig. 2. The Ag substrate temperature was 600°C. The aerosol was generated at a frequency of 1.7 MHz with a power of 50 W. N_2 was used as the carrier gas to minimise the reaction between Ba precursor and CO_2 from air and to avoid the danger of fire. The flow rate was 30 ml/min. Crystalline BaZrO_3 film was formed in a single step without further heat-treatment. The XRD pattern is shown in Fig. 7.

Embodiments of the invention can provide:

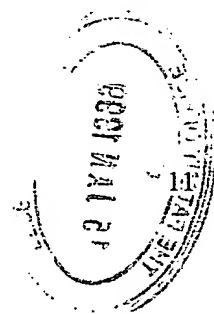
1. A high-efficient film deposition method comprising of

- Generating aerosols with narrow and fine droplet size ($< 2\mu\text{m}$) using an ultrasonic generator operating at a frequency, e.g. above 1.7 MHz with an aerosol-generating rate, e.g. 5 cc/min or higher.
- Depositing charged aerosols preferably upwards through an aerosol nozzle under an electrostatic field to a heated substrate to form dense or porous solid films, multilayers, and compositionally graded and/or composite films. The upwards aerosol nozzle-substrate configuration enable the suitable temperature gradient for chemical reaction near or close to the vicinity of the substrate to form the desired films.
- The substrate can be heated using any heating means. The substrate temperature or thermal environment for the decomposition and/or chemical reactions of the precursor can be adjusted to allow the deposition of the required amorphous and/or crystalline film in a single-step without the need of further heat treatment.
- The DC voltage is preferably below 20 kV. The distance between the nozzle and substrate is preferably less than 5 cm. The deposition temperature is preferably under 800°C . The deposition atmosphere is preferably non-oxide.

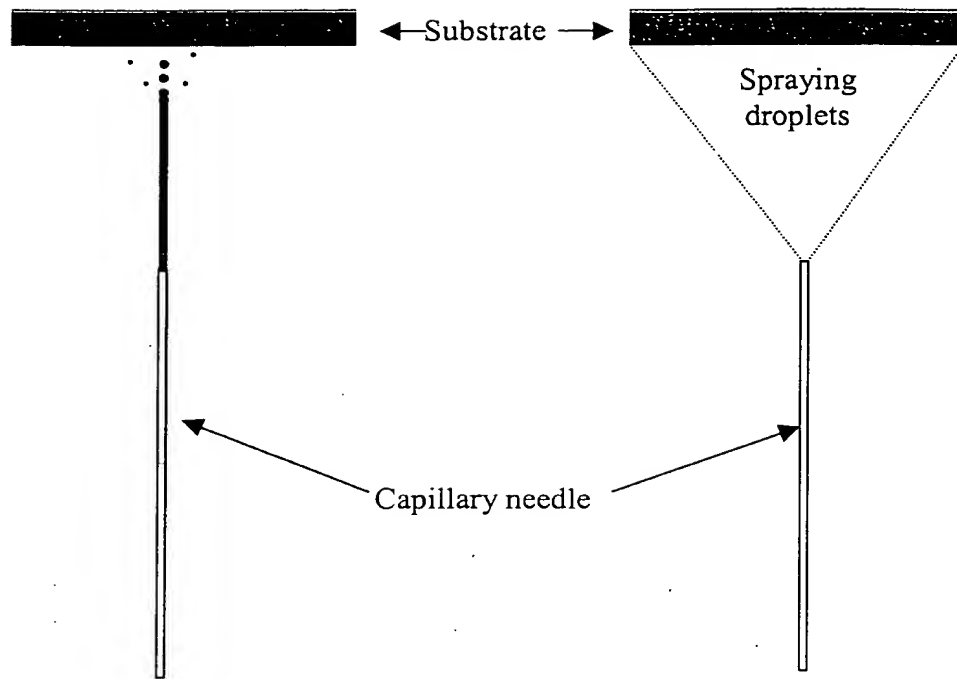
2. An aerosol nozzle according to paragraph 1, which is made of a co-axial tube and a single or multi-tip electrode on a mesh. The tube is made of non-conducting materials (e.g. glass, quartz or ceramic) and the electrode is conducting material (e.g. stainless steel or tungsten).

3. A method according to paragraph 1, wherein an inert and/or reactive gas is used to deliver aerosol to through the aerosol nozzle and/or to react with the precursor during deposition.

4. A method according to paragraph 1, 2 or 3, wherein a computer-controlled X-Y or X-Y-Z table and/or multiple nozzles are used to deposit the films on large area, curved surface or complex shaped engineering components. The substrate can be stationary, rotated and/or translated.
5. A method can be applied for localised deposition by directing the aerosol to the required area of deposition and/or applied electric field between the nozzle and localised substrate.
6. A film with different thickness and surface coverage obtained by the method according to any preceding paragraph wherein said film is derived from both aqueous and non-aqueous solutions. The said film can be thin or thick, simple or multi-component, oxide or non-oxide or hybrid film (e.g. organic/inorganic films) which can be used for any engineering and medical applications.
7. A process which can be performed at atmospheric, high or reduced pressure environment.





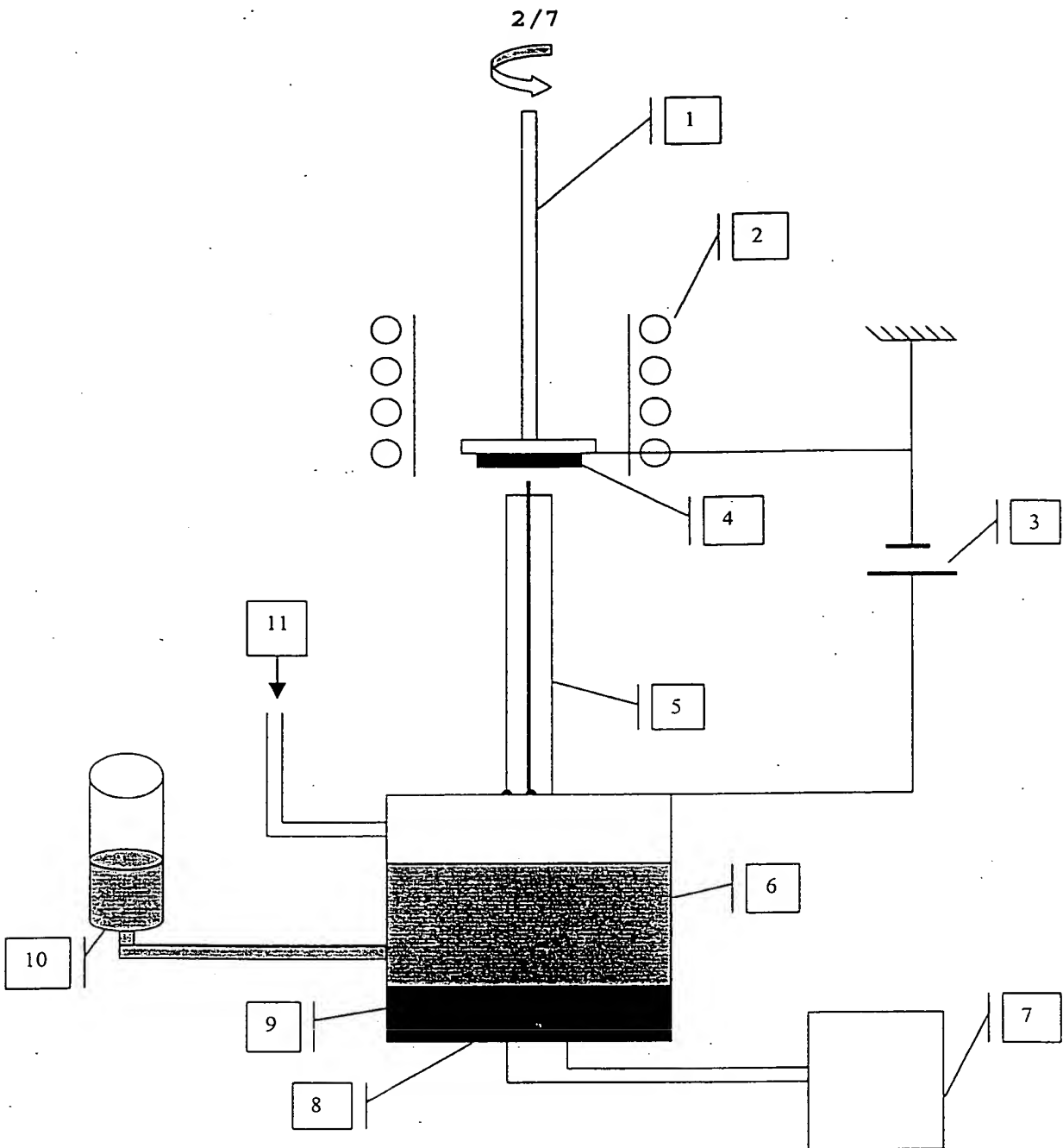


(a) Simple-jet mode

(b) Cone-jet mode

Fig. 1. Two electrostatic spray modes for plate-capillary configuration.

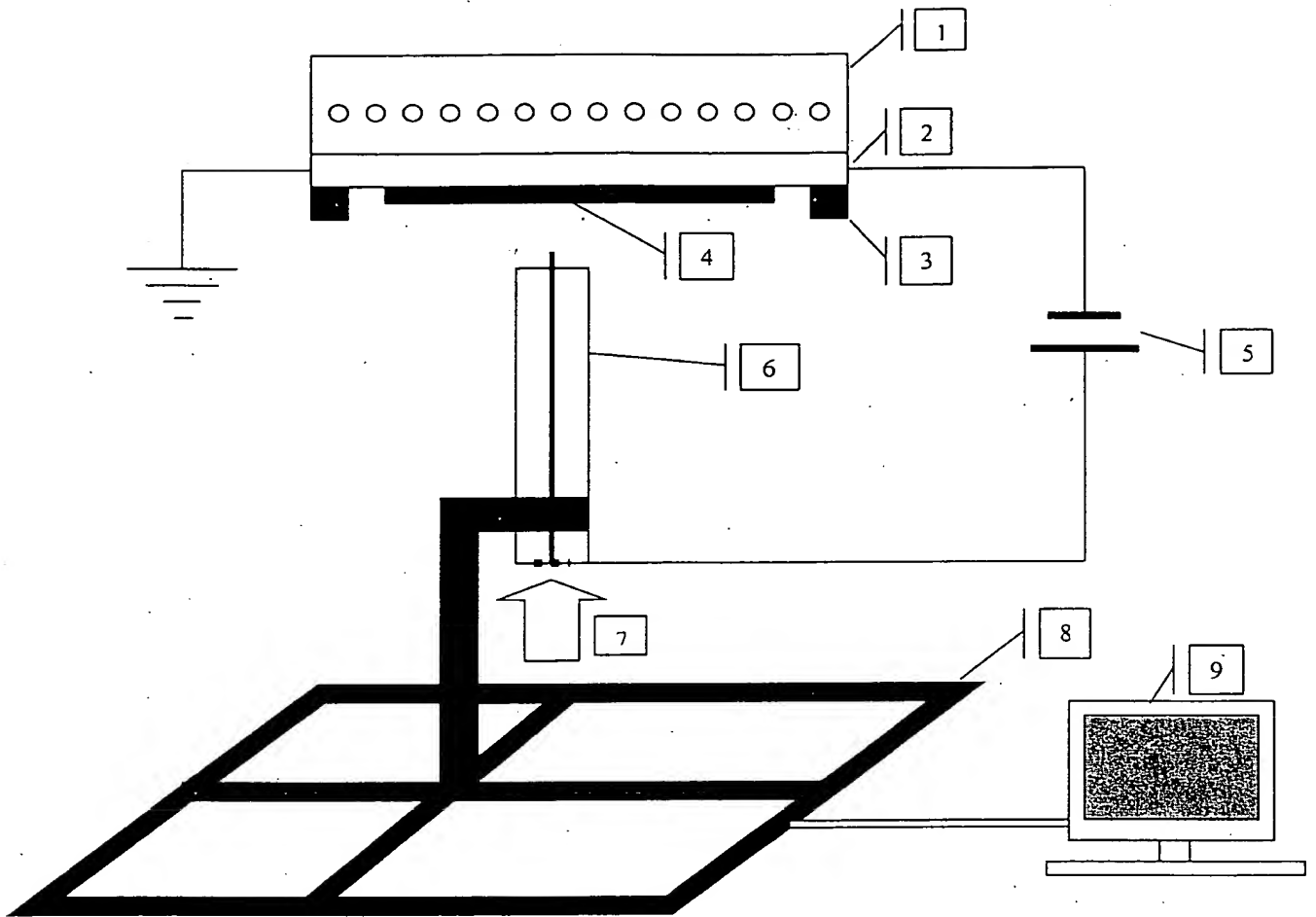




1. Rotary substrate holder
2. Heating element
3. High voltage generator
4. Substrate
5. Aerosol nozzle
6. Precursor solution
7. Ultrasonic generator
8. Piezoelectric transducer
9. Transfer media
10. Liquid level controller
11. Carrier gas

Fig. 2 An example of EAAJD set-up for small area deposition.

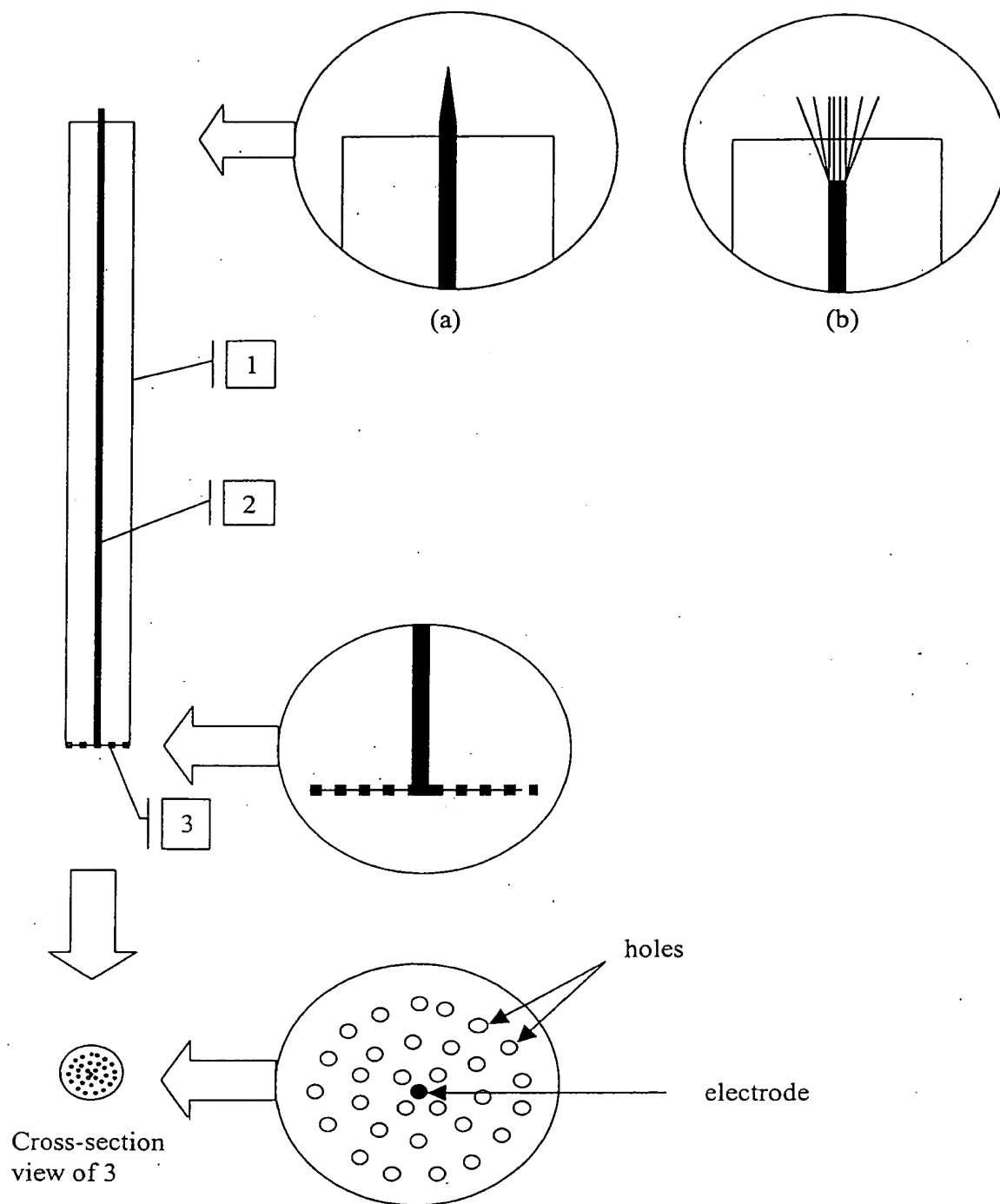




1. Heating element (or infrared lamp)
2. Substrate holder
3. Insulating material
4. Substrate
5. High voltage generator
6. Aerosol nozzle
7. Aerosol
8. X-Y-Z table
9. Computer

Fig.3. An example of EAAJD set-up for large and/or complex-shape deposition.

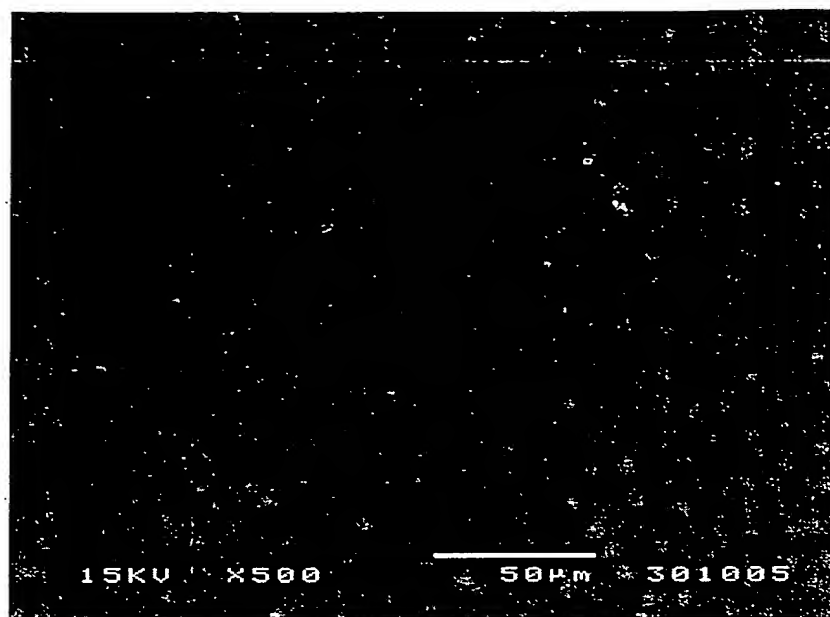




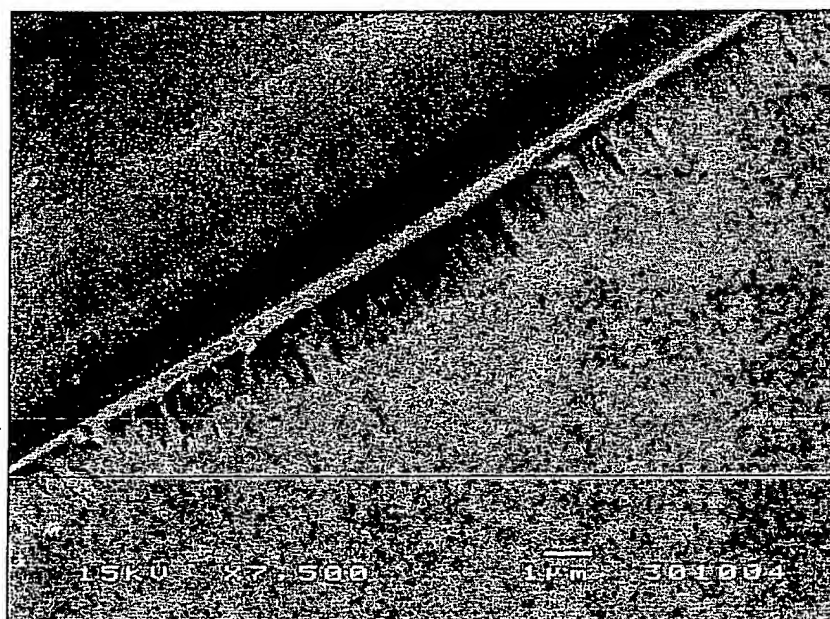
1. Non-conducting tube
2. Conducting electrode
3. Multi-hole mesh

Fig. 4. The set-up of an aerosol nozzle.





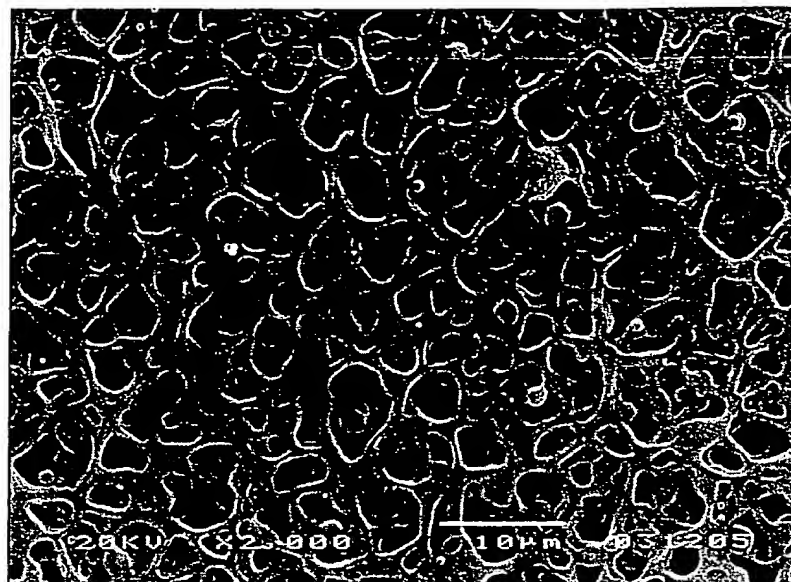
(a) Surface



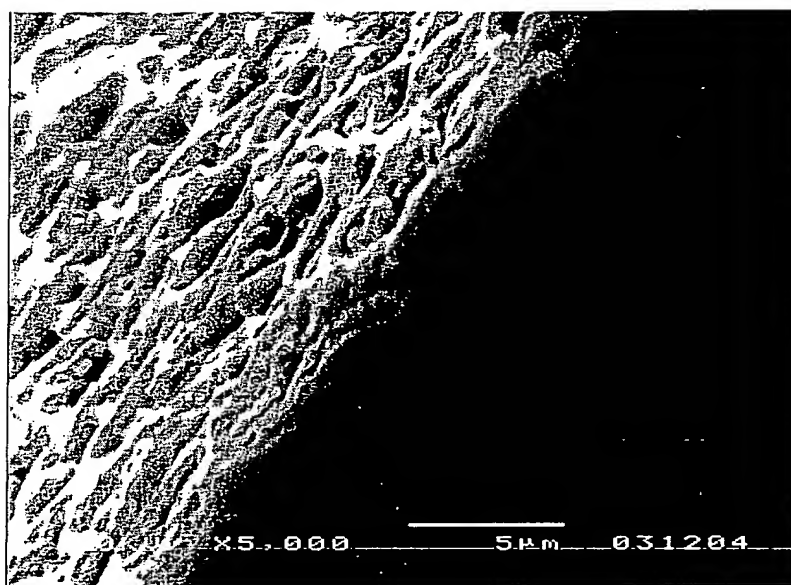
(b) Cross-section

Fig.5. SEM Micrographs of CdS Films deposited at 450°C via EAAJD Technique





(a) Surface



(b) Cross-section

Fig. 6. Porous SiO₂ films deposited at 200°C by EAAJD method



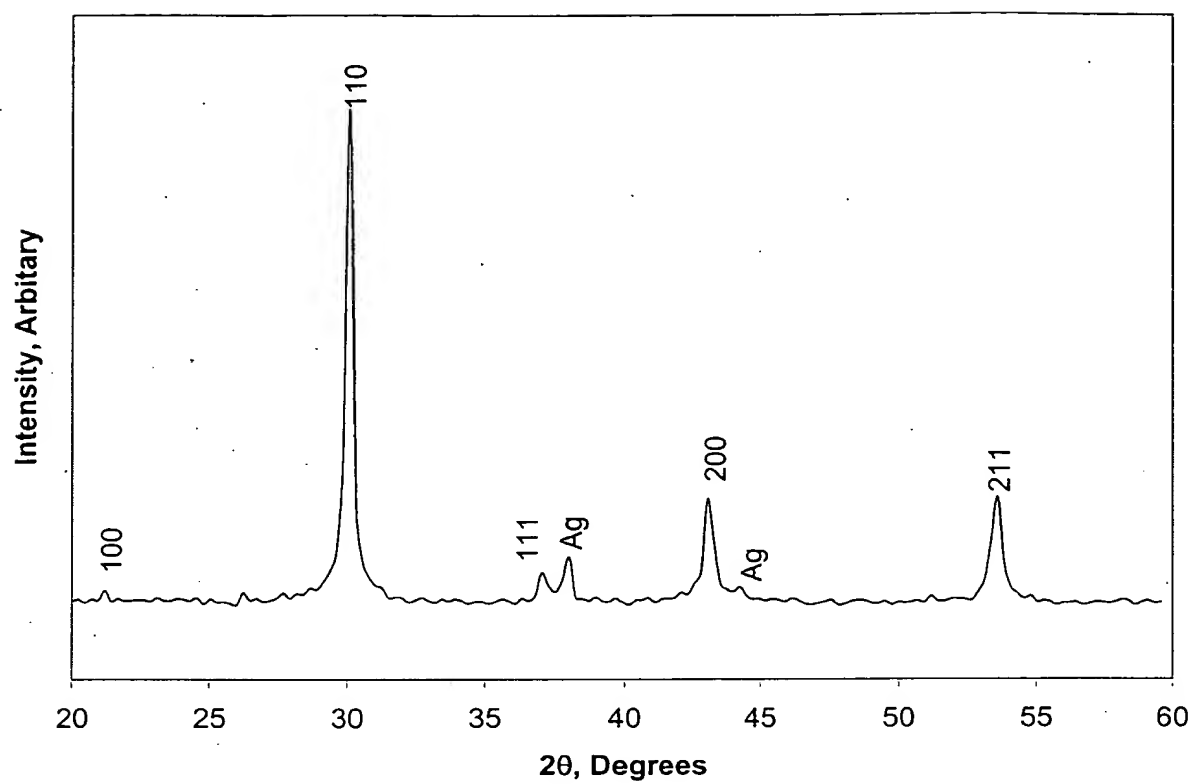


Fig. 7. XRD Pattern of BaZrO₃ film deposited at 600°C via EAAJD technique

